INFLUENCE OF REPLACING SE IN GE$_{10}$SE$_{90}$ GLASSY ALLOY BY 50 AT. % TE ON THE OPTICAL PARAMETERS

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The effect of addition of 50 at.% Te by replacing Se in Ge$_{10}$Se$_{90}$ glassy alloy on the optical parameters has been studied in the present work. Thin films of Ge$_{10}$Se$_{90}$ and Ge$_{10}$Se$_{40}$Te$_{50}$ the glassy alloys were prepared by thermal evaporation technique at a base pressure of ~10^{-6}mbar. Thin films were characterized by X-ray diffraction technique to check the amorphous nature of thin films. Transmission spectra of thin films were taken in the range of 400-1500 nm. The straight forward technique proposed by Swanepoel using transmission spectrum was used to calculate the optical parameters (refractive index and extinction coefficient) of the thin films. The dispersion of refractive index is described in terms of Wemple-DiDomenico single oscillator model. The optical absorption edge is described using non-direct transition model proposed by Tauc and optical band gap (E_g^{opt}) is calculated by Tauc extrapolation. The optical band gap was found to decrease with 50 at.% addition of Te.

1. Introduction

Interest in the optical properties of chalcogenide glasses has been increased due to their potential applications in different areas like switching elements, infrared optical elements, optical fibers, optical transmission media, reversible phase change optical records [1-6] etc. High optical transparency in the near and far infrared region as well as large optical non-linearity are two important and attractive optical properties of chalcogenide glassy semiconductors which are used in linear and non-linear integrated optical elements. Se based chalcogenides have attracted much attention due to their device applications such as rectifiers, photocells, xerography, switching and memory devices [7].

In the present work we have taken the Ge$_{10}$Se$_{90}$ glassy alloy. The addition of third element Te (50 at.%) by replacing Se expands the glass forming region and also creates compositional and configurational disorder in the system [8]. The optical study to calculate refractive index (n) and extinction coefficient (k) is performed for Ge$_{10}$Se$_{90}$ and Ge$_{10}$Se$_{40}$Te$_{50}$ by analyzing the transmission spectra of thin films using envelope method proposed by Swanepoel [9]. The optical band gap is also calculated by Tauc's extrapolation method [10].

2. Experimental

Bulk samples of Ge$_{10}$Se$_{90}$ and Ge$_{10}$Se$_{40}$Te$_{50}$ were prepared by melt quenching technique. Materials (99.999% pure) were weighed according to their atomic percentages and sealed in

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evacuated (at ~ 10^{-6} mbar) quartz ampoules. The sealed ampoules were kept inside a rocking furnace where the temperature was increased up to 1000 ^{o}C at a heating rate of 3-4 ^{o}C/min. The ampoules were frequently rocked during 24 hours at the highest temperature to make the melt homogeneous. The quenching was done in ice + water. The material has been found amorphous in nature as confirmed by x-ray diffraction technique. Thin films of $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ glassy alloys were deposited on cleaned glass substrates by thermal evaporation at ~10^{-6} mbar pressure. The glass substrates were firstly cleaned by soap solution at room temperature using ultrasonic cleaner then with double distilled water, a dip in acetone followed by ethyl alcohol, dried in an oven at approximately 110 ^{o}C. The vacuum evaporation process was carried out in a coating system (HINDHIVAC model 12A4D India). Thin films were also characterized by X-ray diffraction technique and found to be amorphous in nature as no prominent peak was observed in the spectra. The transmission spectrum of the thin films in the spectral range 400 – 1500 nm were obtained using a double beam ultraviolet-visible-near infrared spectrophotometer (Hitachi-330). The spectrophotometer was set with a slit width of 1 nm. It was therefore unnecessary to make slit width corrections as the value of slit width was much smaller than the line widths [11]. All the measurements reported here were carried out at room temperature.

3. Results and discussion

Using the experimental data of optical transmittance of $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films, the refractive index and extinction coefficient are calculated. The homogeneous film has thickness (d) and complex refractive index $n^{*} = n - ik$, where n is the refractive index and k is the extinction coefficient. The thickness of the substrate is several times larger than the thickness of the film. Fig. 1 shows the oscillating curves which indicates that the thickness of the films is constant.
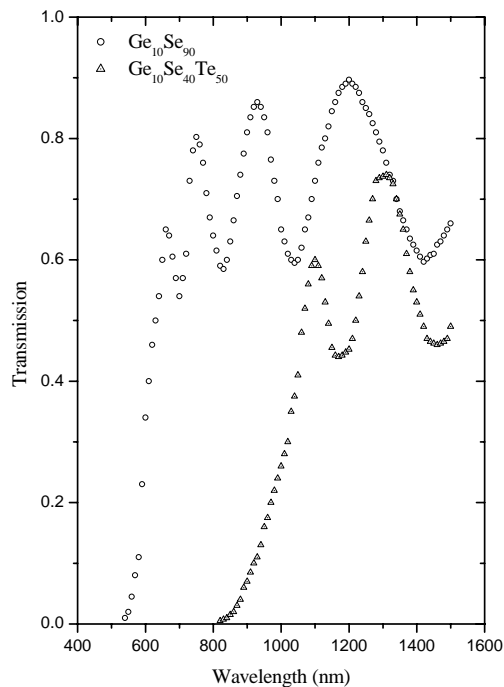

Fig. 1 Transmission spectrum for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films
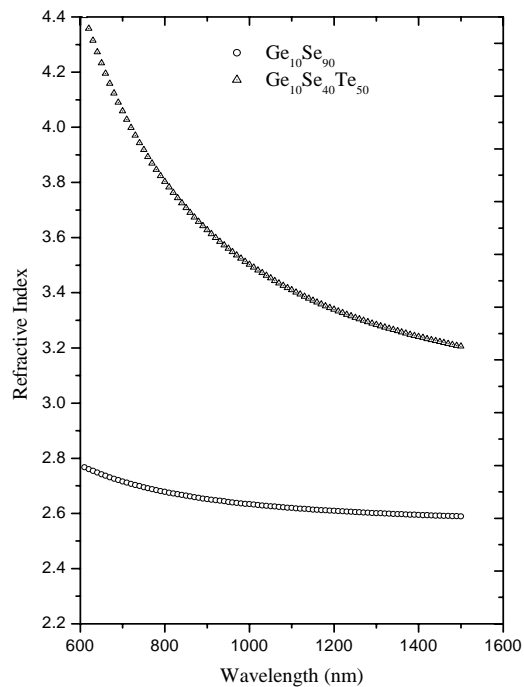
Fig. 2 Plot of refractive index vs. wavelength for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films

The optical parameters were obtained from the fringe pattern in the transmittance spectrum. According to Swanepoel [9] the value of the refractive index of the film can be calculated by using the following procedure.

In the transparent region where the absorption coefficient $\alpha \approx 0$, the refractive index (n) is given by

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \tag{1}$$

where
$$N = \frac{2s}{T_m} - \frac{(s^2 + 1)}{2} \tag{2}$$

and T_m is the envelope function of minimum transmittance and s is the refractive index of substrate.

In the weak region where $\alpha \neq 0$ the transmittance decreases due to the influence of α and the refractive index n is given by

$$n = [M + (M^2 - s^2)^{1/2}]^{1/2} \tag{3}$$

where
$$M = 2s \frac{T_M - T_m}{T_M T_m} + \frac{(s^2 + 1)}{2} \tag{4}$$

and T_M is the envelope function of maximum transmittance. Refractive index can be estimated by extrapolating the envelops corresponding to T_M and T_m. The accuracy of the refractive index can be increased by calculating d taking into account the basic interference equation

$$2nd = m\lambda \tag{5}$$

where $m = 1,2,3...$ at the maximum points in the transmission spectrum
and $m = 1/2, 3/2, 5/2...$ at minimum points in the transmission spectrum.

If n_1 and n_2 are the refractive indices of two adjacent maxima or minima at wavelengths λ_1 and λ_2, then the thickness of the film is given by

$$d = \lambda_1 \lambda_2 / 2(\lambda_1 n_2 - \lambda_2 n_1) \tag{6}$$

In the strong absorption region the transmittance decreases drastically due to the influence of α, and refractive index can be estimated by extrapolating the values calculated in the other regions. The extinction coefficient k can be calculated using the relation

$$k = \frac{\alpha \lambda}{4\pi} \tag{7}$$

where α is the absorption coefficient and is given by

$$\alpha = (1/d)\ln(1/x) \tag{8}$$

where x is the absorbance.
In the region of weak and medium absorption using the transmission maxima, x can be calculated by

$$x = \frac{E_M - [E_M^2 - (n^2 - 1)^3 (n^2 - s^4)]^{0.5}}{(n-1)^3 (n - s^2)} \tag{9}$$

where

$$E_M = \frac{8n^2 s}{T_M} + (n^2 - 1)(n^2 - s^2) \tag{10}$$

The spectral distribution of refractive index and extinction coefficient are shown in Fig. 2 and Fig. 3 respectively. Both refractive index and extinction coefficient were found to decrease with the increase of wavelength for the thin films under investigation.
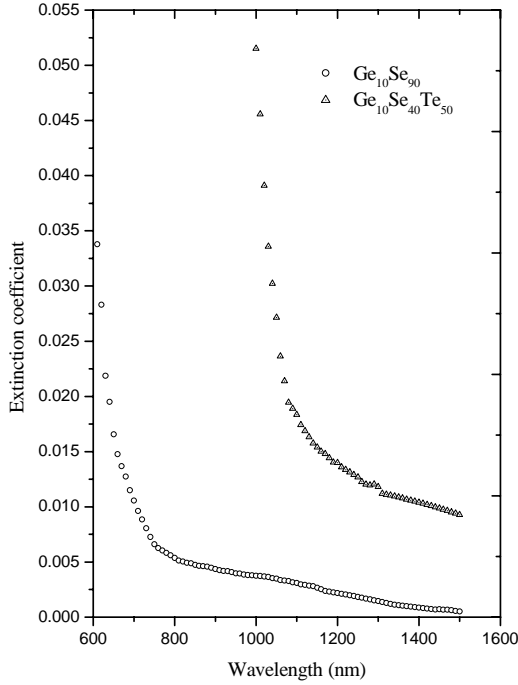
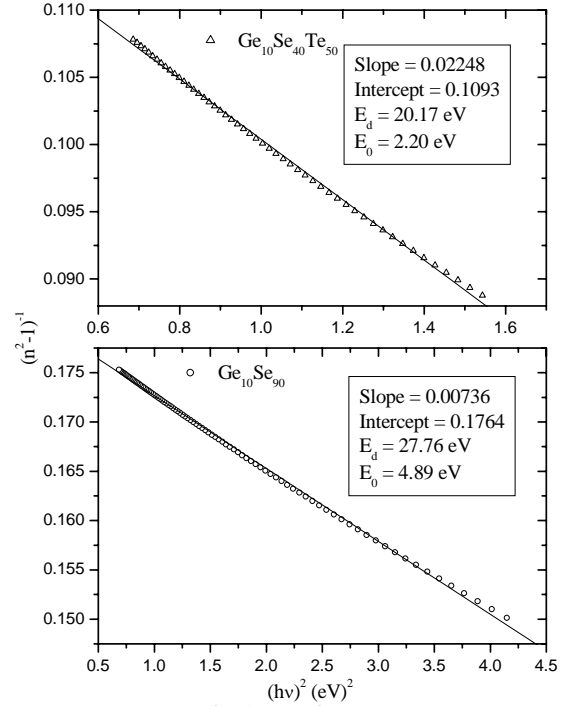Fig. 3 Variation of extinction coefficient with wavelength for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films

Fig. 4 Plot of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films

The high frequency properties of $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films could be treated as single oscillator. According to the single-effective oscillator model proposed by Wemple and DiDomenico [12,13] the optical data could be described to an excellent approximation by the following relation

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - (h\nu)^2} \tag{11}$$

where $h\nu$ is the photon energy, n is refractive index, E_0 is the energy of the effective dispersion oscillator also called average energy gap, E_d is the oscillator strength or the dispersion energy. The latter quantity measures the average strength of the interband optical transitions. Plotting $(n^2 - 1)^{-1}$ against $(h\nu)^2$ allows us to determine the oscillator parameters by fitting a straight line to the points. Fig. 4 shows the plot of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$. The value of E_0 and E_d can be directly determined from the slope $(E_0 E_d)^{-1}$ and the intercept on the vertical axis (E_0 / E_d). The calculated values of E_0 and E_d are given in the inset of Fig. 4. The straight line equation corresponding to least square fit for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films are $(n^2 - 1)^{-1} = 0.1764 - 0.00736 (h\nu)^2$ and $(n^2 - 1)^{-1} = 0.1093 - 0.02248 (h\nu)^2$ respectively. The value of static refractive indices (n_0) for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films are calculated by extrapolating the Wemple-DiDomenico dispersion equation to $h\nu \rightarrow 0$ and the values of n_0 found to be 2.582 and 3.185 respectively. The high frequency dielectric constants [14] $\varepsilon_\infty = (n_0)^2$ for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films are 6.667 and 10.144. Moreover an important achievement of Wemple-DiDomenico model is that it relates the dispersion energy E_d to other physical parameters of the material through a simple empirical relation

$$E_d = \beta N_c Z_a N_e \qquad (12)$$

where N_e is effective number of valence electrons per anion, N_c is effective coordination number of the cation nearest neighbour to the anion, Z_a is the chemical valency of the anion and β is a two valued constant with either an ionic or covalent value (for ionic materials $\beta = 0.26 \pm 0.03$ eV and for covalent materials $\beta = 0.37 \pm 0.04$ eV [12]).

In the high absorption region from which the optical band gap is determined, the absorption is characterized by Tauc's relation [10]

$$\alpha h\nu = B\left(h\nu - E_g^{opt}\right)^n \qquad (13)$$

where $h\nu$, E_g^{opt} and B denotes the photon energy, the optical gap and band tailing parameter respectively. In the above equation $n = 1/2$ for a direct allowed transition, $n = 3/2$ for a direct forbidden transition, $n = 2$ for an indirect allowed transition and $n = 3$ for an indirect forbidden transition. Fig. 5 shows the plot between $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for calculation of optical band gap (E_g^{opt}). The optical gap determined by the intercept of the extrapolations to zero absorption with the photon energy axis $(\alpha h\nu)^{1/2} \to 0$ (Tauc extrapolation [10]). It is clear from Fig. 5 that the optical gap decreases with addition of 50 at.% of Te content. The decrease of the optical gap with Te content can be correlated with the character of the chemical order of chalcogenide amorphous semiconductors. According to the model described by Kastner [15], the dominant contribution for states near the valence band edge in materials having chalcogen atoms as major constituents, comes from chalcogen atoms, especially from their lone-pair p-orbital. The lone-pair electrons in these atoms adjacent to electropositive atoms will have higher energies than those close to electronegative atoms. Therefore, the addition of electropositive elements to the alloy may raise the energy of some lone-pair states sufficiently to broaden further the band inside the forbidden gap. The electronegativities of Ge, Se and Te are 1.8, 2.4 and 2.1 respectively. According to these values, it is noticed that Te is less electronegative than Se, so the substitution of Te for Se may raise the energy of some lone-pair states and hence broaden the valence band. This will give rise to additional absorption over a wider range of energy leading to band tailing and hence shrinking of the band gap. The optical gap decreases from 1.87 to 1.03 eV for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films respectively. The addition of Te in the glass structure causes deeper band tails extended in the gap and thereby leading to a decrease in the value of optical band gap.
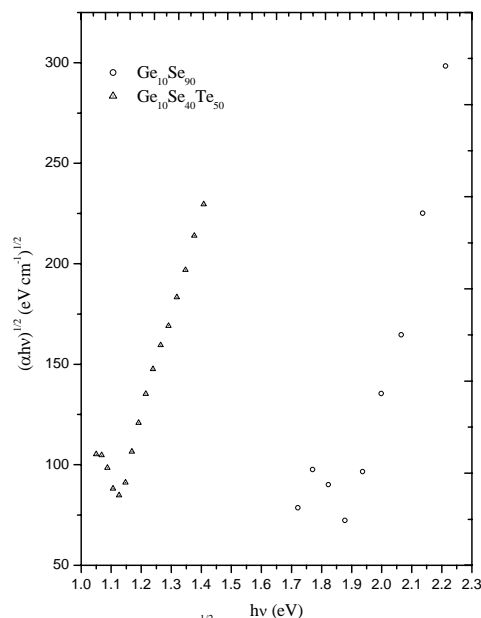

Fig. 5 Plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films

The decrease of optical band gap with increasing Te content may also be related to the increase number of Ge-Te (37.4 kcal/bond), Se-Te (40.6 kcal/bond) and Te-Te (33.0 kcal/bond) bonds and decrease of Se-Se (44.0 kcal/bond) and Ge-Se (49.1 kcal/bond) bonds. The strength of Ge-Te, Se-Te and Te-Te bonds is lower as compare to Ge-Se and Se-Se bonds so the optical absorption edge shifts towards higher values of wavelength with the addition of Te. Tellurium enters into the tetrahedral structure of $GeSe_2$ forming units containing all the three elements (Ge, Se, Te) thus leading to the modification of the glassy network. Further, the optical band gap is strongly dependent on the fractional concentration of Te atoms. This may be due to the tendency of Te atoms to form chemical disordering and to create localized states in the forbidden gap [16] leading to lower the optical band gap.

4. Conclusions

The transmission spectra of $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films were analyzed in the range of 400-1500 nm for the calculation of optical parameters. Refractive index and extinction coefficient decrease with the increase of wavelength. The optical band gap obtained by Tauc's extrapolation is 1.87 and 1.03 respectively for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films. The decrease in optical band gap is explained on the basis of bond energy and chemical disordering. The values of static refractive indices are found to be 2.582 and 3.185, respectively. The high frequency dielectric constants for $Ge_{10}Se_{90}$ and $Ge_{10}Se_{40}Te_{50}$ thin films are found to be 6.667 and 10.144, respectively.

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